

METHOD OF HIGHLY SENSITIVE ANALYSIS OF
NUCLIDES BY MULTIPLE GAMMA-RAY DETECTION

BACKGROUND OF THE INVENTION

5 This invention relates to the application of multiple
gamma-ray detection to qualitative and quantitative
determination of radionuclides or nuclides in samples
radioactivated by neutrons or other particle rays or gamma-
rays. The multiple gamma-rays emitted from the nuclides
are measured simultaneously and information is taken for a
10 pair of gamma-rays from each nuclide, thereby analyzing the
nuclides at higher resolution than the conventional
measurement of gamma-rays.

15 According to the invention, concurrent gamma-rays
emitted from radionuclides are counted simultaneously with
a multiple gamma-ray detector assembly consisting of a
plurality of gamma-ray detectors to make a two-dimensional
matrix, which is analyzed to ensure that the nuclides of
interest are separated completely and analyzed
simultaneously.

20 The resolution that can be achieved by the prior art
method of analysis has been about 1,000 and this is
increased by a factor of 1,000 to 1,000,000 in the improved
method of the invention which analyzes a two-dimensional
matrix. This resolution is high enough to enable complete
25 separation of nuclides in a sample no matter how many they
are. Consider an unreal situation where a maximum of 2,000
- 3,000 nuclides known today are generated simultaneously
in an accelerator or a reactor; since they each generate

about 10 gamma-rays on the average, the maximum total number of gamma-rays that are emitted is on the order of 10,000 but given the resolution of 1,000,000, their amounts can be determined simultaneously by analysis of a two-
5 dimensional matrix according to the invention.

In the conventional analysis of radioactivity, gamma-rays emitted from radionuclides are measured with a single unit of germanium semiconductor detector to obtain a one-dimensional energy spectrum and the nuclides of interest
10 are identified on the basis of energy and half-life information. The resolution by the germanium detector is about 1,000 at 1 MeV. The number of gamma-rays emitted from one radionuclide is on the order of ten at average and there is no problem with a sample containing a limited
15 number of nuclides. However, a sample containing several tens of nuclides emit as many as several hundred gamma-rays and it is impossible to separate them completely. In particular, weak gamma-rays are blocked by strong gamma-rays and cannot be analyzed.

20 To analyze non-radioactive samples, they are first radioactivated by particles from an accelerator or a reactor and the gamma-rays emitted from the sample are detected (for qualitative analysis) and their intensity is measured (for quantitative analysis). In this neutron
25 radioactivation analysis method, the sample of interest is radioactivated by neutrons from a reactor and the gamma-rays emitted from the sample are measured with a single unit of high-resolution germanium detector to produce a

one-dimensional spectrum which is analyzed for peaks,
thereby performing quantitative determination.

The analyses described above have been conducted in
many fields by various methods and the radioactivation
5 analysis method has seen particularly wide use. Since the
development of the germanium semiconductor detector in the
sixties, radioactivation analysis using gamma-rays capable
of high-resolution detection has made great advances and it
is now possible to quantify trace elements in various
10 samples including environmental samples, bio-samples and
samples for use in space and earth science studies.

Fig. 1 shows a conventional method of gamma-ray
measurement by radioactivation. A sample 1 radioactivated
by thermal neutrons from a reactor emits gamma-rays which
15 are measured with a single unit of germanium detector 2 to
construct a one-dimensional spectrum 3 plotting count
(intensity) on the vertical axis and the energy of gamma-
rays on the horizontal axis. If the sample contains many
elements, this method yields such a complex spectrum that
20 it is often difficult to measure the elements of interest
in separate form.

A major problem of the prior art methods is their
high susceptibility to interference by concomitant
nuclides. If you are lucky enough, there is no overlap
25 between gamma-rays but if the sample contains many
nuclides, the spectrum has such a high background that it
is very difficult to detect weak gamma-rays.

To eliminate the adverse effects of interfering

nuclides, samples such as spent nuclear fuels that contain many nuclides are usually subjected to chemical separation or differentiation of nuclides by half-life. However, chemical separation usually requires special skills and
5 prolonged time; in addition, it is necessary to determine the yield of chemical separation but this can be a source of errors. Differentiation by half-life is not an ideal method, either. Considerable time is taken to determine the quantity of a nuclide of long half-life and it is quite
10 cumbersome to maintain the detector system throughout that period.

Thus, the conventional techniques are highly susceptible to the interference by concomitant nuclides and samples such as environmental samples that contain
15 many elements have to be subjected to chemical separation in order to eliminate the adverse effects of the interfering nuclides. For chemical separation, its yield must be determined and this in turn necessitates re-radioactivation; hence, chemical separation requires
20 special skills and prolonged time but this can be a source of errors.

In the conventional method of radioactivation analysis, a sample radioactivated by neutrons from a reactor is measured with a single unit of germanium
25 detector to construct a one-dimensional spectrum and the peaks in the spectrum are analyzed to determine the quantities of elements in the sample. If the sample contains many elements, the relative intensity of generated

radioactivity is not distributed among all nuclides present but assigned to only limited nuclides and it is difficult to identify trace elements without chemical separation; however, errors in the percent efficiency of recovery
5 achieved after separation not only affect the result to be finally obtained, separation also requires sophisticated skills of chemical analysis.

In the method of neutron radioactivation analysis, the relative intensity of generated radioactivity is not
10 generally distributed among all nuclides present but assigned to only limited nuclides and it is often difficult to perform simultaneous analysis of many trace elements. For example, bio-samples have strong radioactivity from ^{24}Na , ^{56}Mn , ^{42}K and ^{82}Br and geological samples from ^{24}Na , ^{56}Mn ,
15 ^{42}K , ^{46}Sc and ^{59}Fe ; hence, in the method of analyzing a one-dimensional spectrum with a single detector unit, the peaks of short-lived nuclides are masked by these strong nuclides and cannot be detected. To deal with this problem, radioactivity measurement has to be performed after strong
20 radioactive nuclides are removed by chemical separation. This not only requires sophisticated skills of chemical analysis; after chemical separation, re-radioactivation has to be performed in the reactor to determine the percent recovery of the desired nuclide. A further concern is the
25 possibility that the precision of analysis may be affected by the process of chemical separation.

SUMMARY OF THE INVENTION

Noting that many radioactive nuclides emit a

plurality of gamma-rays, the present inventors devised a method of qualitative and quantitative determination of these nuclides by analyzing a two-dimensional matrix obtained by measuring them with a multiple gamma-ray
5 detector assembly consisting of a plurality of gamma-ray detectors. The method achieved 1,000 times as high an energy resolution as the conventional method of analyzing a one-dimensional spectrum.

The two-dimensional matrix method of the invention
10 comprises the steps of detecting a plurality of concurrent gamma-rays from radioactive nuclides in a sample with two or more detectors in a multiple gamma-ray detector assembly, cumulatively adding the energies of a pair of detected gamma-rays on a two-dimensional matrix, and
15 detecting the peaks. The background of a one-dimensional spectrum is localized in a two-dimensional plane, being limited to less than 10 counts in almost all regions; hence, even very weak peaks are sufficiently detected to achieve higher detection sensitivity.

20 In addition, the method of the invention does not require chemical separation or any other artificial operations and, hence, can be performed on-line with a computer. Once preliminary calibration has been done for the energy of each detector and the efficiency of
25 detection, a two-dimensional matrix is generated as the sample is measured; the position of a particular peak on the matrix tells the nuclide it represents and, at the same time, with reference to the nuclear data for each nuclide

that is stored in the computer, the quantity of the particular nuclide is determined from the intensity of the peak and real-time display of the result is possible. Needless to say, the quantities of nuclides having long
5 half-life can be determined at high speed.

Similarly, the present invention enables qualitative and quantitative analyses of the nuclides in samples that have been radioactivated with neutrons from an accelerator or a reactor.

10 BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows a conventional method of gamma-ray detection as applied to a radioactivated sample;

Fig. 2 shows the invention method of gamma-ray detection as applied to a radioactivated sample; and

15 Fig. 3 shows a two-dimensional matrix constructed by the invention method of gamma-ray detection.

DETAILED DESCRIPTION OF THE INVENTION

(1) Qualitative and quantitative analyses of nuclides in a sample radioactivated with neutrons

20 Using a multiple gamma-ray detector assembly consisting of a plurality of germanium semiconductor detectors, a plurality of gamma-rays emitted from a radioactivated sample are measured and combinations of two simultaneously observed gamma-rays are recorded in a
25 computer and then analyzed to construct a two-dimensional matrix. Combining a gamma-ray having a given energy with a concurrently observed gamma-ray, one can construct a neat spectrum which is substantially free from the interference

by gamma-rays from dissimilar nuclides. As a result, there is no need to perform artificial operations such as chemical separation and still gamma-rays from trace elements can be measured without interference by gamma-rays from concomitant nuclides.

Fig. 2 shows the invention method of gamma-ray detection as applied to a sample 1 radioactivated with thermal neutrons from a reactor. Gamma-rays simultaneously emitted from the sample are measured by simultaneous counting with a multiple gamma-ray detector assembly 4 to construct a two-dimensional matrix 5 which plots the count (intensity) on the vertical axis, the energy of one gamma-ray on the horizontal axis, and the energy of the other gamma-ray on an axis in between the two axes. According to this method, two gamma-rays γ_1 and γ_2 emitted simultaneously from a radioactive nuclide in the sample are measured simultaneously with the multiple gamma-ray detector assembly to construct the two-dimensional matrix rather than a one-dimensional spectrum. As a result, even a sample containing many nuclides can be analyzed for gamma-rays at a resolution of 1,000 without chemical separation or any other artificial operations and this achieves measurement of nuclides in completely separate form. The nuclide of interest can be identified by the position determined by the coordinates (γ_1 , γ_2) on Fig. 2 and the amount of its abundance is detected by the height (count) of the peak in that position.

As Fig. 3 shows, radioactivated ^{152}Eu generates two

gamma-rays simultaneously, one having an energy of 841.6 keV and the other at 121.8 keV. These two gamma-rays were subjected to simultaneous counting with the multiple gamma-ray detector assembly to construct a two-dimensional matrix.

Fig. 3 also shows a graph plotting the energies of the two gamma-rays on the horizontal and vertical axes. The inset for the range of 100 - 140 keV on the vertical axis and the range of 820 - 860 keV on the horizontal axis is shown enlarged below the graph. As is clear from the enlarged inset, the two gamma-rays from ^{152}Eu having respective energies of 121.8 keV and 841.6 keV were recorded simultaneously and the identity of the nuclide that emitted those gamma-rays could be known by their positions. In this way, the quantities of as many as 49 elements could be determined simultaneously in resolutions up to the ppb (10^{-9}) order.

The multiple gamma-ray detector assembly used in the present invention has such a high detection efficiency that samples taken in quantities on the milligram order suffice for measurement purposes. Since the method of analysis of the invention is nondestructive, radioactivated samples can be subjected as such to measurement and this provides not only great convenience but also applicability to a wide range of samples. For example, the method has potential applications in the quantitative determination of trace metal elements in environmental and bio-samples, as well as in earth science and space science for analysis of

meteorites.

Dating techniques using ^{129}I (half life of 1.57×10^7 yr) and ^{244}Pu (8.08×10^7 yr) have recently been proposed and the method of this invention can be applied to analyze

5 these nuclides. Knowledge is increasing about the relationship between the concentrations of trace elements in living organisms and their biological functions. Since the method of the invention is capable of measuring a wide range of elements simultaneously, it can be used to
10 determine the quantities of heretofore unidentifiable trace elements so that their effects are studied for the first time.

(2) Qualitative and quantitative analyses of nuclides in a radioactive sample

15 Using a multiple gamma-ray detector assembly consisting of a plurality of gamma-ray detectors, a plurality of gamma-rays emitted simultaneously from a radioactive sample were measured and energy information about a pair of emitted gamma-rays was recorded in a
20 computer for each event and then analyzed to construct a two-dimensional matrix. Intensity measurement was done on the matrix. Alternatively, a narrow gate may be set on one of the two axes, one-dimensional spectra are sliced and the intensities of two-dimensional peaks are effectively
25 measured. By preliminary calibration of the energies of gamma-rays and their intensities, the channels and areas of the two-dimensional peaks can be transformed to energy and intensity, respectively. Based on these data, one can

perform quantitative determination of nuclides.

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The procedure described can be performed on-line if the detectors are preliminarily calibrated against a standard radiation source. Specifically, a standard radiation source with known energy and intensity is measured and calibration data for energy and detection efficiency are prepared for each detector. As an actual sample is measured, each detector is calibrated for energy so as to construct a two-dimensional matrix. At the same time, the nuclear data for each nuclide that are stored in the computer are referenced to determine the quantities of nuclides from the intensities of peaks in the matrix on the basis of the calibrated data for detection efficiency, whereby the result is displayed on a real-time basis. Needless to say, the quantities of long-lived nuclides can be determined without waiting for the disappearance of short-lived nuclides and this permits faster analysis.

The multiple gamma-ray detector assembly to be used in the invention consists of at least two gamma-ray detectors. Signals from the two detectors are fed to a fast simultaneous counter which chooses only simultaneous counting events. At the same time, the energy information from the two detectors is taken into the computer. On the basis of this information, the correlation between two gamma-rays is represented on a two-dimensional matrix by means of a frequency distribution of events. The two-dimensional matrix may be replaced by any suitable equivalents. The performance of the multiple gamma-ray

detector assembly improves with the increasing number of
detector units and the increasing detection efficiency of
each detector unit. If necessary, the multiple gamma-ray
detector assembly may be combined with a BGO suppressor to
5 suppress the background and provide higher sensitivity.

The following examples are provided for the purpose
of further illustrating the present invention.

Example 1: Quantitative Determination of Trace Elements by
Neutron Radioactivation Method

10 Standard rock samples were irradiated with neutrons
in a reactor and the gamma-rays from the radioactivated
samples were measured with a multiple gamma-ray detector
assembly. The gamma-rays emitted from about 100 mg of each
sample that had been radioactivated for 10 minutes in the
15 reactor were measured with the multiple gamma-ray detector
assembly for about 4 days. Specifically, standard rock
samples JB-1 and JP-1 published by the Geological Survey of
Japan, Agency of Industrial Science and Technology, MITI
(now the National Institute of Advanced Industrial Science
20 and Technology), were irradiated with neutrons in JAERI
Research Reactor JRR-4 and subjected to a four-day
measurement with a multiple gamma-ray detector assembly
"GEMINI" in the tandem accelerator facilities at JAERI
Tokai Research Establishment.

25 The measurement started immediately after the neutron
irradiation and the quantities of as many as 27 nuclides
could be determined simultaneously within a short time; no
artificial operations such as chemical separation were

performed and there was no need to wait for the decay of short-lived nuclides. The contents of the measured elements as calculated from the intensities of gamma-rays agreed with the documented values within the range of errors. The same technique could perform simultaneous quantification of 49 elements. Since the two-dimensional matrix had such a reduced amount of background that it allowed for detection of very weak peaks and the relative abundances of nuclides that could be determined quantitatively were on the order of 10^{-9} (one billionth).

The multiple gamma-ray detector assembly "GEMINI" used in Example 1 was a spherical array of anti-Compton gamma-array detectors each being the combination of a BGO Compton suppressor and a germanium detector and capable of lower background and higher resolution. GEMINI was completed in July 1998 and its primary objective is to measure gamma-rays from highly excited atomic nuclei produced by various nuclear reactions and to investigate their internal structures. GEMINI has achieved many results in nuclear spectroscopic experiments using heavy ion beams at JAERI Tokai tandem accelerator facilities.

The forty-nine elements that could for the first time be quantitated simultaneously by the new detection method of the invention were the following: Ag, As, Ba, Br, Ca, Cd, Ce, Cl, Co, Cs, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, I, In, Ir, K, La, Lu, Mn, Mo, Na, Nd, Ne, Ni, Os, Pt, Ra, Rb, Re, Ru, Sb, Sc, Se, Sm, Sn, Ta, Tb, Th, Ti, U, W, Yb and Zn; the detection limits of these elements were 10^{-2} to 10^{-3} on a

weight basis.

On the other hand, the conventional radioactivation method of analysis (using a one-dimensional spectrum) was capable of simultaneous quantification of the following
5 twenty-three elements: Al, Ar, Au, Cr, Cu, Dy, F, Ho, Kr, Mg, Nb, Pd, Pr, Rh, S, Sr, Te, Tl, Tm, V, Xe, Y and Zr; the detection limits of these elements were 10^{-2} to 10^{-3} on a weight basis.

Example 2: Analysis of Actinides

10 Obtaining basic data for the nuclear transformation of minor actinides constitute an important basic portion of nuclear research. The quantification of minor actinides which is necessary for this purpose has primarily relied upon the measurement of alpha-rays. Alpha-rays need be
15 detected in high resolution since nuclides of similar atomic numbers emit alpha-rays of similar energies. However, alpha-rays lose so large amounts of energy as they pass through a medium that it has been necessary for the sample to be first subjected to chemical separation to
20 remove impurities, then dried out and processed into a thin radiation source. This has not only required special skills, it has sometimes been difficult to achieve high enough separation efficiency.

These problems are free from the multiple gamma-ray
25 detection method and high-precision analysis can be accomplished without chemical separation although the method requires the emission of multiple gamma-rays. As a matter of fact, in the measurement of ^{237}Np standard

radiation source using GEMINI, nuclides of intensities as low as 0.01 Bq could be measured in complete isolation from other nuclides.

Geological samples irradiated with neutrons usually
5 emit strong gamma-rays from ^{24}Na and ^{56}Mn , making it
difficult to measure gamma-rays from trace elements. The
multiple gamma-ray analysis method of the invention could
perform simultaneous measurement of gamma-rays from 27
elements without chemical separation. The contents of the
10 measured elements as calculated from the intensities of
gamma-rays agreed with the documented values of the
standard rock samples within the range of errors.

These results show that the invention is applicable
not only to qualitative analysis but also to quantitative
15 analysis. Among the elements detected, Eu was present in a
very small amount of 4 ppb but it could still be measured
together with other elements without chemical separation.
Given more favorable conditions, the method is applicable
to the detection of 49 elements.

20 A multitude of radionuclides contained in a sample
cannot usually be determined quantitatively in a completely
separated state for the purpose of quantitative
determination. The multiple gamma-ray detection method
used in the invention achieves much higher resolution than
25 the conventional method and the nuclides in the sample, no
matter how many they are, can be separated and quantified
completely without employing chemical separation or other
ancillary means.